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Blue Luminescence of Facial Tris(quinolin-8-olato)aluminum(III) in Solution, Crystals, and Thin Films**

By *Michele Muccini*,* *Maria Antonietta Loi*, *Kester Kenevey*, *Roberto Zamboni*, *Norberto Masciocchi*, and *Angelo Sironi*

The first efficient low-voltage-driven organic light-emitting devices (OLEDs), reported by Tang and VanSlyke,[1] were based on tris(8-hydroxyquinoline)aluminum(III) (Alq_3). Fifteen years later, Alq_3 is still a key compound widely investigated and used in electroluminescent devices. Significant improvements have been achieved in device efficiency and stability,[2] and efforts have been made to tune the green emission typical of Alq_3 OLEDs using multilayer structures and chemical doping.[3]

The class of trischelate oxyquinoline octahedral metal complexes (Mq_3), of which Alq_3 is a member, may exist in the *fac* or *mer* isomeric forms, of C_3 and C_1 symmetry, respectively. Through the years, *mer*-Mq_3 molecules have been extensively characterized in the solid state, the only example of a non-*mer* molecule being Sbq_3,[4] which, however, is not octahedral due to the presence of a stereochemically active lone pair. Only very recently, the blue-light-emitting *fac*-Alq_3 isomer was prepared and characterized by X-ray powder diffraction (XRPD).[5,6]

Even before the preparation of pure *fac*-Alq_3 powders, the fundamental importance and the possible technological implications of Alq_3 isomerization has prompted an intense experimental and theoretical effort.[7,8] *mer*-Alq_3 crystallizes in the α and β phases (and in a number of clathrates), whose optical properties are determined by the nature of π–π intermolecular contacts.[9] Partial crystallographic information concerning a high-temperature phase, referred to as γ, has previously been reported.[9] A blue-shifted emission was found for *fac*-Alq_3, in the so-called δ phase.[8] With the aim of clarifying the phase field stability, the nature of the photoluminescence (PL) properties, the phase-transformation processes, and the possible reversibility of molecular isomerization, we eventually discovered how to selectively produce in large quantities, starting from the commercially available α-Alq_3 material, the γ- and δ-Alq_3 phases (both containing the less stable *fac*-isomer), as well as solutions of *fac*-Alq_3, from which blue-light-emitting films can be prepared.

α-Alq_3 polycrystalline powders can be easily transformed into the γ phase upon heating at ca. 400 °C under atmospheric pressure. We have now discovered that a few drops of liquid acetone promote, at room temperature (RT), the quantitative γ to δ phase transformation, whereas seeding supersaturated *mer*-Alq_3 solutions with γ (or δ) nuclei does not yield the δ phase, suggesting that γ- and δ-Alq_3 share the same (facial) isomer.

Conventional ^1H and ^{13}C NMR investigations at RT reveal that, regardless of the starting material (α, γ, or δ phases), only the *mer*-Alq_3 species is present in solution. Intramolecular ligand scrambling in the *mer* isomer has been recently studied by dynamic NMR in $CDCl_3$ solution (283–310 K temperature range).[10] This study, besides estimating the activation parameters for the *mer*/*mer* and *mer*/*fac* interconversions, confirmed the impossibility of directly observing *fac*-Alq_3 resonances at room temperature.

However, we show in Figure 1a that pure *fac*-isomer can be observed when γ- or δ-Alq_3 are suspended in $CDCl_3$ at –50 °C. The *fac*-Alq_3 isomer shows a simpler ^1H NMR spectrum due to its C_3 symmetry. It consists of two multiplets centered at about δ 8.36 ppm (H4) and δ 7.52 ppm (H6) and of many severely overlapped peaks, ranging from 7.1 to 7.4 ppm (H2, H3, H5, and H7). All H2 atom resonances are shifted upfield as the 'unique' H2 of *mer*-Alq_3 (δ 7.22 ppm).[11]

The spectra reported in Figure 1a show that the *fac*-isomer in solution progressively transforms into *mer*-Alq_3 on increasing the temperature, and indicate that the isomerization initiates at ca. –20 °C.[12] The *fac*-Alq_3 is inert at –50 °C for several hours and starts to slowly convert in *mer*-Alq_3 at –20 °C, in agreement with the kinetic parameters derived by Utz et al.[10,13] Figure 1b shows the ^1H NMR spectra in the 6.5–8.5 ppm range collected at –10 °C over an interval time of 120 min, showing the progressive *fac*- to *mer*-Alq_3 isomerization in isothermal conditions. The transformation diagram that relates the *mer* and *fac*-isomers in solution and in the solid state is reported in Figure 2.

The PL spectra of *mer*- and *fac*-Alq_3 solutions are reported in Figure 3. The optical emission of *fac*-Alq_3 in solution at –50 °C is centered at 2.59 eV and has a bright blue color. The spectral position of the PL does not change at temperatures below –20 °C, while it begins to shift towards lower energy at higher temperatures. The emission maximum reaches a minimum energy value of 2.36 eV. This demonstrates that the blue-light emission is a molecular property and is not determined by the crystal packing in γ and δ phases. In addition,

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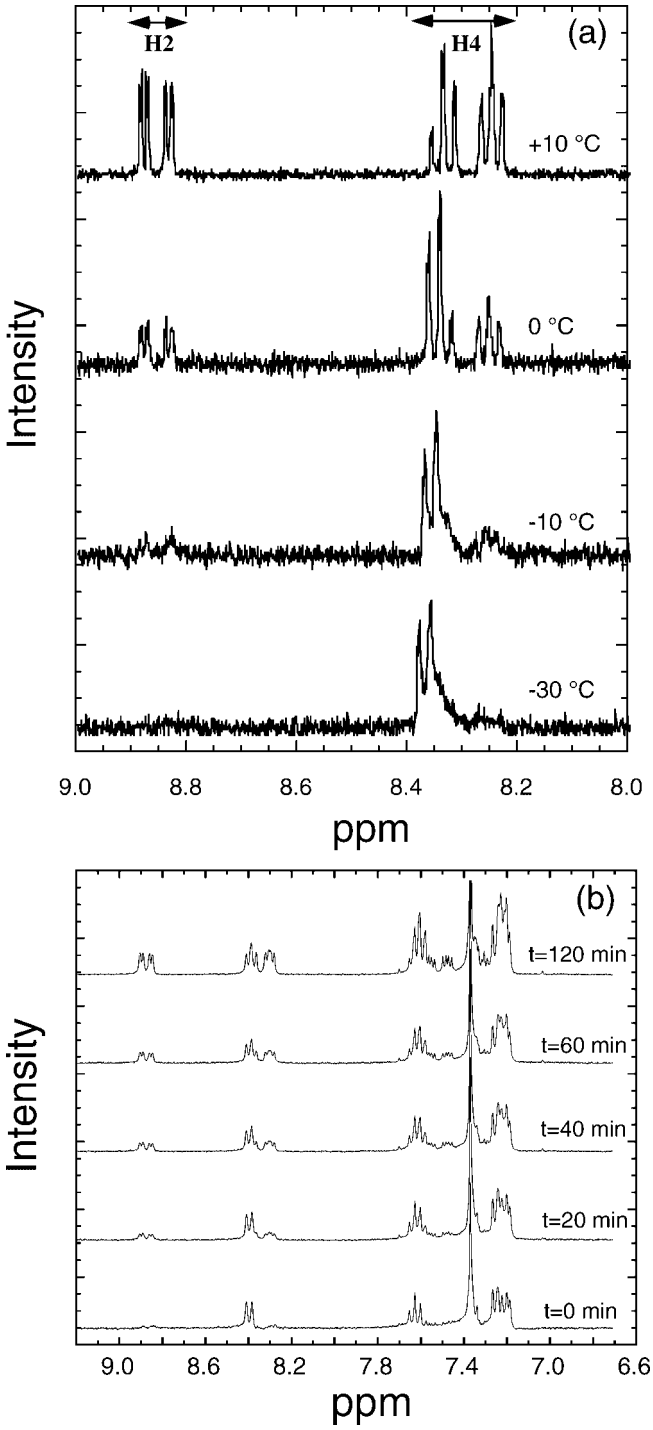

Figure 1. a) ^{1}H NMR spectra (in the 8–9 ppm range) of δ-Alq_3 dissolved in $CDCl_3$ at –50 °C, measured at different increasing temperatures. The absence of the 'unperturbed' H2 signals (near δ 8.9 ppm) in the lower trace, coupled with the fact that only the signals of three *magnetically equivalent* H4 nuclei are observed, shows that only the *fac*-isomer is present at –30 °C. b) Time evolution of the ^{1}H NMR spectra (6.5–9.5 ppm range) of δ-Alq_3 (dissolved in $CDCl_3$ at –50 °C), measured *isothermally* at –10 °C. Peaks of the *mer*-isomer progressively appear with time. The increase of the overall proton resonance intensities as well as of the signal-to-noise ratio observed during isomerization is due to the higher solubility of *mer*-Alq_3, which induces the progressive dissolution of suspended δ-Alq_3.

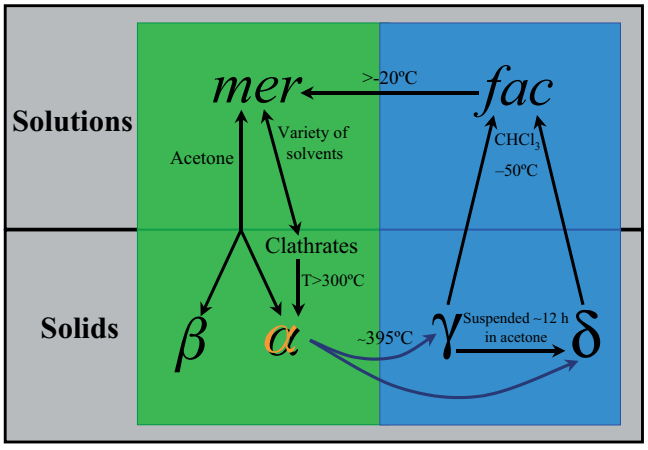

Figure 2. Phase-transformation diagram of the four distinct solid phases of unsolvated Alq_3 based on two different geometrical isomers. The *fac*-isomer can only be obtained by a solid-state reaction (blue arrows). However, dilute solutions of the *fac*-isomer can be prepared from the δ (or γ) phase at low temperatures, since it is kinetically stable in solution below –20 °C.

the above observation is consistent with the results of NMR spectroscopy, which indicate, at temperatures higher than –20 °C, a facile *fac* to *mer* conversion and a negligible concentration of the *fac* isomer in equilibrium with *mer*-Alq_3. Thus, the PL spectral emission provides a distinctive fingerprint of each isomer. The experimental energy difference of 0.23 eV between the PL spectra of *mer*- and *fac*-Alq_3 in solution is in close agreement with the value of 0.3 eV predicted by Curioni et al. by ab initio quantum chemical calculations.[7f]

Using an integrating sphere interfaced with a cryostat for temperature control,[14] the PL quantum yield of *fac*-Alq_3 dissolved in $CHCl_3$ was measured at –50 °C. The solution was then heated and maintained at RT to allow complete isomerization to *mer*-Alq_3. The PL quantum efficiency of the *fac*-isomer was 20 ± 3 % compared to 32 ± 2 % determined for *mer*-Alq_3. The higher uncertainty in the determination of the *fac*-Alq_3 quantum yield is due to its very low solubility. Despite the lower quantum yield of *fac*-Alq_3, its value is sufficiently high to be of interest as an emitting chromophore.

As mentioned above, according to ab initio calculations, the *mer* isomer is ca. 4 kcal mol^{-1} more stable than the *fac* in the gas phase. If we assume that this (i.e., a [*fac*]/[*mer*] Boltzmann ratio in the 10^{-3}–10^{-4} range) is also true in solution, we can easily explain why the solution chemistry of Alq_3 is dominated by the *mer* isomer: i.e., no sizable amounts of *fac*-Alq3 can be obtained by solution chemistry from *mer*-Alq3. This result is in agreement with early ^{1}H NMR investigations, which revealed only the *mer* isomer at all investigated temperatures.[11] In contrast, the *mer* to *fac* transformation easily occurs in the solid state at ca. 400 °C when starting from the α phase; the formation of a 'less stable' molecular species is not surprising, since a more favorable lattice free energy may overcome such small energy differences. Differential scanning calorimetry (DSC) mea-

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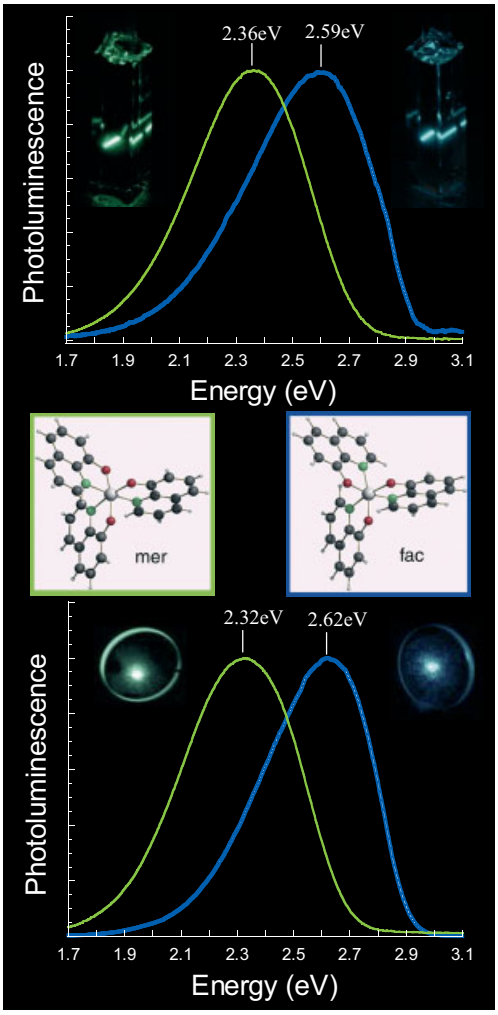

Figure 3. Top: *mer*-Alq_3 solution and *fac*-Alq_3 solution (–50 °C) illuminated by an ultraviolet laser beam and corresponding PL spectra. The insets show the molecular structures of the *mer*- and *fac*-isomers. Bottom: *mer*- and *fac*-Alq_3 films illuminated by a UV laser beam, and corresponding RT PL spectra.

surements suggest the weak exothermic nature of this transformation, possibly related to the larger molecular dipole of the *fac*-isomer,[7f] i.e., to more favorable dipole–dipole interaction in the solid (see below). In addition, γ-Alq_3 has a larger molecular volume and, consequently, a molar entropy higher than that of the α phase.

Remarkably, the γ phase, which is indefinitely stable in the solid state, readily transforms into the δ phase at RT if acetone is added, through a solid–solid, solvent mediated, phase transformation. Acetone grants limited mobility to the *fac* molecules, which crystallize as the denser, more stable, δ phase, well in advance of isomerization (which occurs on the milliseconds timescale[10]). Despite several attempts (and a number of systematic modifications of the reported procedure), we have not succeeded in preparing pure δ-Alq_3 by the method described in the literature.[6,15] Invariably, and consistently with the first reported preparation of the blue-light-emitting Alq_3 material,[8] mixtures of γ- and δ-Alq_3 phases were always found (X-ray powder diffraction (XRPD) evidence). In contrast, our original DSC analysis,[9] which allowed the discovery of the γ-Alq_3 phase, matches the features highlighted in Figure 1 of Cölle et al.[15]

XRPD analysis (see Experimental) shows that the two phases are correlated by a proper group–subgroup relation, the δ phase[5,6] being simply obtained by removing the threefold axes (in $P\bar{3}$) of the γ phase while maintaining all inversion centers. As a consequence, epitaxial growth of δ- (triclinic $P\bar{1}$) on top of γ-Alq_3 is possible. α-, γ-, and δ-Alq_3 share comparable lattice parameters, indicating that different isomers can adopt very similar packing modes. The common motif is the presence of chiral $[Alq_3]_\infty$ columns, running parallel to the shortest axis, (pseudo)trigonally packed in the plane normal to it. In all phases, due to their centrosymmetric nature, (±)Alq_3 molecules, hence enantiomeric columns, coexist in an equimolecular ratio. This implies that in all cases the favorable motif of antiparallel chains of dipoles is present. Interestingly, the rather short π–π contacts between adjacent oxyquinolines, observed in the α-, β-Alq_3, and in a number of clathrates of the *mer*-isomer, are absent in the *fac*-Alq_3 containing phases.

The slight difference in the crystal packing of γ- and δ-Alq_3 is reflected in their Raman spectra, which show the same intramolecular phonon modes, but different lattice modes.[16] Consistently, the γ- and δ-Alq_3 optical emission spectra are identical.

Thermally sublimed thin films always display green luminescence, irrespective of the crystalline phase and isomeric form of the starting material. The possibility of preparing stable blue-light-emitting thin films of Alq_3 follows from the understanding of the Alq_3 isomerization and of the phase-transformation diagram. The availability of stable *fac*-Alq_3 solutions, at $T < -20$ °C, allows the preparation of films by spin-coating on RT substrates, since solvent evaporation is faster than isomerization. Figure 3 shows films obtained by spin-coating from *fac*- and *mer*-Alq_3 solutions on quartz substrates and their (blue and green) RT PL spectra. These are featureless even at low temperature as a consequence of the amorphous nature of Alq_3 thin films. PL spectra of γ- and δ-Alq_3 polycrystalline powders show, at low temperature, the same vibronic progression as α-Alq_3,[9] with a Huang–Rhys factor of about 2.6. This indicates that the same strong electron–phonon coupling is present in both the *fac*- and *mer*-isomers for the radiative electronic transition.

In conclusion, we report on the isolation, mass production, and characterization in solution and in the solid state (as two polymorphic phases and films) of the facial stereoisomer of the Alq_3 molecule. A phase transformation diagram, which reveals how to produce selectively the two polymorphs of the *fac*-isomer (γ- and δ-Alq_3) via a solid-to-solid reaction, is also reported.

In perspective, the availability of blue-light-emitting Alq_3 films, which are stable at RT, may open the route to the development of blue-light-emitting Alq_3-based OLEDs. This, to-

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gether with a more thorough knowledge of the optical and electronic properties of Alq_3, may allow the use of a single active material for red–green–blue (RGB) full-color-display applications.

Experimental

Preparation of γ-Alq₃: α-Alq_3 (Aldrich) was heated to 395 °C, employing a heating ramp of 10 °C min^{-1} over the 50–350 °C range and of 1 °C min^{-1} from 350 °C to 395 °C. After maintaining this temperature for a few minutes the system was rapidly cooled to RT. Resulting dark yellow powders were shown to contain a mixture of the γ-Alq_3 and δ-Alq_3 phases by XRPD analysis. Using 15 mg of starting α-Alq_3 powder, the γ-Alq_3/ δ-Alq_3 ratio was approximately 10:1 and was found to be unaffected by increasing the heating rate to 10 °C min^{-1} or by decreasing the cooling rate to 1 °C min^{-1}. Furthermore, this ratio was maintained on heating to the maximum pre-sublimation temperature of 410 °C. Scaling up to gram starting quantities, however, typically yielded lower γ-Alq_3/δ-Alq_3 ratios.

Preparation of δ-Alq₃: γ-Alq_3 was suspended in acetone for 15 h at RT with occasional stirring. Separation of the resulting light yellow colored powder was achieved by centrifugation. XRPD analysis showed δ-Alq_3 accompanied by < 4 % residual γ-Alq_3. Neither the solvent volume nor the γ-Alq_3/ δ-Alq_3 ratio in the starting powder had any influence on the resulting γ-Alq_3/ δ-Alq_3 ratio.

NMR Spectroscopy: α-, γ-, and δ-Alq_3 powders, dissolved in $CDCl_3$ at RT, afford identical ^{1}H NMR spectra, assigned, in agreement with previous reports [11,17], to *mer*-Alq_3. A distinctive feature of this spectrum is the 'anomalous' lowering (1.5 ppm) of the chemical shift of one of the three H2 atoms. This is due to the unique *intramolecular* environment of this H2 atom, which points towards an adjacent aromatic ring. In a second series of NMR experiments (Bruker NMR AVANCE 400 MHz instrument), solid δ-Alq_3 was cooled to liquid-nitrogen temperature in an NMR sample tube. $CDCl_3$ was then added and the temperature raised to –50 °C at a controlled rate over a 30 min period. A series of ^{1}H NMR spectra was measured at this temperature, which demonstrated the absence of molecular isomerization even after several hours. Spectra were then collected as a function of increasing temperature at 10 °C intervals until RT had been reached. Ten minutes were allowed for stabilization between each measurement (see Fig. 1a). In a third series of experiments (Bruker DXS 300 MHz instrument) reported in Figure 1b, we monitor the isomerization under isothermal conditions (–10 °C).

Thermal Characterization: γ- and δ-Alq_3 phases melt, in a closed vial, near 415 °C, affording a yellow glassy material of unknown isomeric composition while, in open environment, they afford by sublimation needles of the α-phase. Therefore the original *fac*-molecules isomerize, in the gas phase, to *mer*-Alq_3.

PL and Quantum Yield (QY) Measurements: The excitation wavelength for photoluminescence experiments was the 363 nm line of a UV-extended argon-ion laser, and PL was detected using an optical multichannel analyzer. The QY measurements were performed in a calibrated integrating sphere that allows temperature controlled photoluminescence efficiency measurements [12]. For the QY determination, absorption measurements were also performed at the selected temperature (–50 °C for *fac*-Alq_3 solutions, and room temperature for *mer*-Alq_3 ones).

XRPD Analysis: Indexing of the γ-Alq_3 diffraction pattern confirmed the reported trigonal metrics [9] [$a = 14.364$, $c = 6.208$ Å; $M(22) = 42$, $F(22) = 56$ (0.009, 43)]. Structure solution was achieved using simulated annealing and Rietveld refinement by Topas V2.0 (Bruker AXS). Oxyquinoline fragments were treated as rigid groups. On the basis of the complete Rietveld analysis, the correct trigonal space group is not $P\bar{3}1c$ [9], but $P\bar{3}$ (00l reflections being obscured by accidental overlap). Crystal data: $C_{27}H_{18}AlN_3O_3$, M_w 459.43 g mol^{-1}, trigonal, $P\bar{3}$, $a = 14.3807(6)$, $c = 6.2107(4)$ Å; $V = 1112.3(1)$ Å^3, $Z = 2$; $\rho_c = 1.371$ g cm^{-3}; Cu Kα, $\lambda = 1.5418$ Å, R_{wp} and R_p 0.133 and 0.102 for 3501 data, $5 < 2\theta < 75°$, R_B 0.037 for 9 structural and 12 non-structural parameters. CCDC deposition No. 207158. Further spectroscopic and crystallographic details are supplied as Supporting Information.

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[12] The full spectra, supplied as Supporting Information, show also the resonances of C**H**Cl_3 (δ 7.28, s), $\mathbf{H}_2O$ in $CHCl_3$ (δ 1.7, s), and of traces of cyclohexane (δ 1.3, s) and silicone. Note that the C**H**Cl_3 resonance nicely acts as an internal standard, thus demonstrating the progressive increase of the dissolved material upon raising the temperature.
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